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Separation of Zirconium-95 and Niobium-95 by Solvent Extraction using Trifluoroacetylacetone and Benzoyltrifluoroacetone

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The separation of ^{95}Zr and ^{95}Nb by the solvent extraction was studied using trifluoroacetylacetone or benzoyltrifluoroacetone as a chelating reagent. Zirconium is almot completely extracted with benzene from 0.1~0.5*N* H_2SO_4 solution containing 0.1 % H_2O_2 and 0.5*M* trifluoroacetylacetone, or with 0.1*M* benzoyltrifluoroacetone-benzene from 0.3~0.5*N* H_2SO_4 solution containing 0.1 % H_2O_2, whereas Nb remains in aqueous layer, showing the DF value of 5×10^2~2×10^3 or 1~1.5×10^2, respectively. These procedures have such advantages that the pH control is not needed and salt-free ^{95}Nb tracer can be obtained as well as ^{95}Zr tracer. Especially the procedure using trifluoroacetylacetone is very useful, because the extraction equilibrium is rapidly attained, Zr is readily stripped into 4*N* H_2SO_4 solution, and the reagent is easily decomposed by fuming with H_2SO_4.

INTRODUCTION

In the previous research[1], the separation of zirconium-95 and niobium-95 was carried out by the solvent extraction using acetylacetone as a chelating reagent. When the extraction was made by shaking an aqueous solution containing 5 % acetylacetone with equal volume of benzene at pH 5~7, 97% or more of zirconium-95 was extracted into the organic phase, while niobium-95 almost quantitatively remained in the aqueous phase, with the decontamination factor of 3×10^2~1×10^3. Although the method is useful to the separation of these two nuclides and would be available to the preparation of carrier-free zirconium-95 tracer, there are some inconvenient points ; that is, it is impossible to obtain salt-free niobium-95 solution, and it is also troublesome to control pH value especially in handling a strong radioactive solution.

Trifluoroacetylacetone and benzoyltrifluoroacetone show lower pK_D value than acetylacetone, because a trifluoromethyl group increases the acidity of the enol form. The extraction with these chelating reagents would be conducted at a lower pH region or in mineral acid solution, and therfore it may improve the separation method using acetylacetone. From this point of view the extraction behaviour of zirconium and niobium was investigated using these fluorinated β-diketones, and procedure for the separation of zirconium-95 and its daughter nuclide, niobium-95 were proposed.

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APPARATUS AND MATERIALS

The counting of gamma-rays to determining the extractability were made with a Kobe Kogyo NaI (Tl) $\left(1\frac{3''}{4}\times 2''\right)$ well type scintillation counter, Model PS-300, connected to a scaler, Model SA-230, and the absorption curves of beta-rays were obtained with a Metro automatic decatron scaler, Model D-5, using a Philips halogen quenched G-M tube 18505 and with a Kobe Kogyo set of aluminum absorbers, Model EA-21. A Hitachi-Horiba glass electrode pH meter, Model M-3 was used for the pH measurements.

Zirconium- niobium-95 mixture in 0.5 % oxalic acid solution was supplied from The Radiochemical Center, Amersham, England. It was converted to sulphate solution by fuming with sulphuric acid, with or without carrier. Zirconium-95*1 and niobium-95 tracer solution (about 1 μC/ml.) were prepared by Moore's TTA extraction method[2], as described in the previous paper[1], and the radiochemical purities were confirmed by the absorption curves of beta-rays.

Zirconium carrier solution (10 μg/ml.) was prepared by fusing zirconium oxide with potassium bisulphate, followed by dissolving with 2N sulphuric acid. Niobium carrier solution (10 μg/ml.) was made by dissolving niobium metal with sulphuric acid and hydrogen peroxide.

Reagent grade trifluoroacetylacetone, benzoyltrifluoroacetone and thenoyltrifluoroacetone (TTA) were used without further purification. Trifluoroacetylacetone was dissolved in water to make 1M aqeous solution ; benzoyltrifluoroacetone was dissolved with extracting organic solvent to give 0.1M solution ; and TTA was employed as 0.5M benzene solution.

Organic solvents such as chloroform, benzene and butyl acetate were purified by the same way as in the previous experiment[1]. All other reagents were also the reagent grade.

EXPERIMENTAL RESULTS AND DISCUSSION

Extraction Behaviour with Trifluoroacetylacetone

The extraction behaviour of zirconium and niobium was studied by the following procedure : One milliliter of zirconium-95 solution or of niobium-95 solution (about 1 μC/ml.) and 1 ml. of carrier solution (10 μg/ml.)*2 are taken in a 50 ml. separating funnel. Definite amount of sulphuric acid, 1 ml. of 1 % hydrogen peroxide solution*3 and 5 ml.*4 of 1M trifluoroacetylacetone aqueous solution are added, and then the final volume is adjusted to 10 ml. with water. The resulting solution is shaken with 10 ml. of benzene, chloroform or butyl acetate for several minutes (2, 5, 10 or 15 min.). Two milliliters of counting

*1. Zirconium-95 tracer must be freshly prepared every day to minimize the contamination of build niobium-95.

*2. The carrier solution is not taken in the carrier-free extraction.

*3. In the absence of hydrogen peroxide, large parts of niobium is lost from liquid phase (organic and aqeuous layers) by shaking.

*4. Except in the study on the effect of the reagent concentration.

sapmles are pippeted from each of organic and aqueous layers into a test tube (14 mm. in diameter), and the gamma activities are measured with the NaI (Tl) well type scintillation counter. From the data per cent extraction is calculated.

Extraction curves (plot of per cent extraction against acidity) of zirconium were shown in Fig. 1 and Fig. 2. Zirconium is almost quantitatively extracted

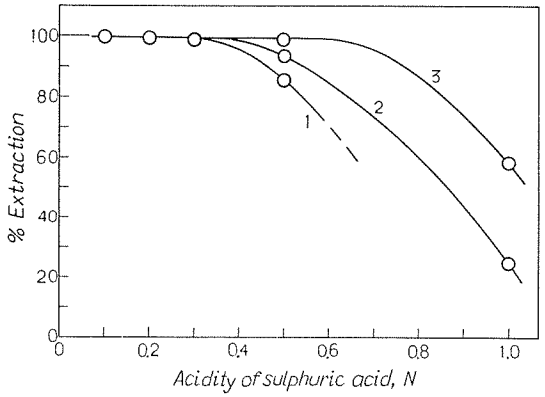

Fig. 1. Extraction curves for Zr-trifluoroacetylacetone-benzene system shaking : curve 1, 2 min. ; 2, 5 min. ; 3, 10 min.

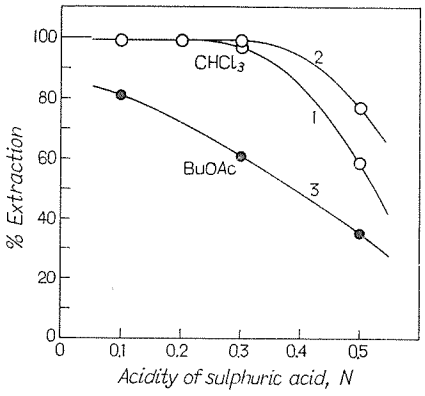

Fig. 2. Extraction curve for Zr-trifluoroacetylacetone-chloroform and butyl acetate systems shaking : curve 1, 2 min. ; 2, 5 min. ; 3, 15 min.

from 0.1~0.5N sulphuric acid medium with benzene or from 0.1~0.3N sulphuric acid medium with chloroform, but the extraction with butyl acetate does not give a satisfactory result. When the extraction is made at lower acidity than 0.1N or in pH region, a partial loss of zirconium is observed, although the date were omitted. It may be attributed to the formation of colloidal hydroxide resulted from the weaker chelating affinity of trifluoroacetylacetone. Figure 3 showed the effect of the reagent concentration. The result indicates that the

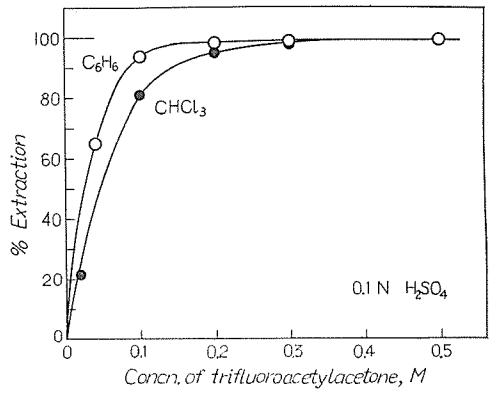

Fig. 3. Effect of concentration of trifluoroacetylacetone.

concentration of trifluoroacetylacetone must be more than 0.3*M* for the complete extraction of zirconium and that benzene is somewhat more suitable than chloroform ; the latter fact is also known by comparing Fig. 1 to Fig. 2. The influence of hydrogen peroxide on the behaviour of zirconium was not revealed within the concentration studied (0.1 % or less).

Extraction behaviour of niobium was also examined. As in the case of acetylacetone, niobium is not extracted and remains completely in aqueous phase under the condition which is optimum for the extraction of zirconium (0.5*M* trifluoroacetylacetone, 0.1~0.3*N* sulphuric acid and 0.1 % hydrogen peroxide). The decontamination factor of niobium for ziconium are 5×10^2~2×10^3 with benzene and 1×10^2 with chloroform.

The back extraction of zirconium was made by shaking organic phase with equal volume of sulphuric acid or of sulphuric acid containing oxalic acid, after extracted from 0.1*N* sulphuric acid solution. As shown in Table 1, zirconium can be easily stripped into 4*N* sulphuric acid.

Table 1. Back extraction of Zirconium.

Solvent	Stripping solution	% Back extn.
C_6H_6	2*N* H_2SO_4	95.0
	4*N* H_2SO_4	99.3
	6*N* H_2SO_4	99.5
	2*N* H_2SO_4+5% Ox. Acid.	100
$CHCl_3$	2*N* H_2SO_4	96.3
	4*N* H_2SO_4	99.7
	6*N* H_2SO_4	99.7
	2*N* H_2SO_4+5% Ox. Acid.	99.7

Extraction Behaviour with Benzoyltrifluoroacetone

The extraction of zirconium and niobium were performed as follows : A 10 ml. of aqueous sample solution having a desired acidity and containing about 1 1 μC of zirconium-95 or niobium-95 with 10 μg of the carrier (except in the carrier-free experiment) and 0.1 % hydrogen peroxide is shaken with 10 ml. 1*M* benzoyltrifluoroacetone-organic solvent solution. Shaking follows for from 10 minutes to 1 hour, and the extractability is estimated by the gamma counting as in the extraction using trifluoroacetylacetone.

The extraction curves of zirconium and effect of shaking were shown in Fig. 4 and Fig. 5, respectively. From the results it is deduced that the shaking must be continued at least for 45 minutes, and then more than 98 % of zirconium can be extracted with 0.1*M* benzoyltrifluoroacetone-benzene from 0.3~0.5*N* sulphuric acid solution containing 0.1 % hydrogen peroxide. As the extracting solvent, benzene is superior to chloroform or butyl acetate ; with chloroform the extraction recovery of zirconium not exceed 90 %, even when the shaking follows for one hour under the optimum condition ; and with butyl acetate the extraction is far from being quantitative. Zirconium is readily back extracted from

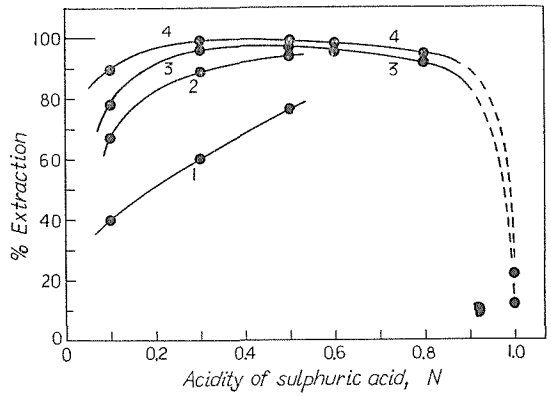

Fig. 4. Extraction curves for Zr-benzoyltrifluoroacetone-benzene system shaking : curve 1, 10 min. ; 2, 20 min. ; 3, 30 min. ; 4, 45 min. (60 min.).

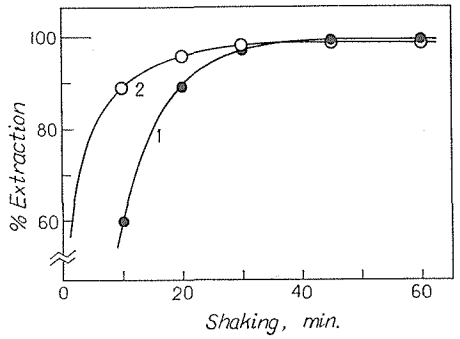

Fig. 5. Effect of shaking period [Zr-benzoyltrifluoroacetone-benzene system] curve 1, 0.3N H_2SO_4 ; curve 2, 0.5N H_2SO_4.

benzene into 6N sulphuric acid solution.

Niobium can not be extracted with 0.1M benzoyltrifluoroacetone-benzene in the acidity range studied (0.1~0.8 N sulphuric), and gives the decontamination factor of $1\sim1.5\times10^2$ for zirconium.

Separation of Zirconium-95 and Niobium-95

From the above results it seemed to be possible that the extractions using these fluorinated β-diketones were adapted to the separation of zirconium-95 from niobium-95, therfore the following procedures were designed.

Using trifluoroacetylacetone : To 2~3 ml. of zirconium- niobium-95 mixture solution*5 taken in a separating funnel, 1 ml. of 1N sulphuric acid, 1 ml. of 1 % hydrogen peroxide solution and 5 ml. of 1M trifluoroacetylacetone solution are added, and the solution is shaken with 10 ml. of benzene for about 5 minutes. After the organic phase is separated and washed twice with 10 ml. of 0.1N sulphuric acid containing 0.1 % hydrogen peroxide, zirconium-95 is back extrated into 5ml. of 4 N sulphuric acid, which is evaporated to almost dryness,— Zirconium-95 fraction. The aqueous phase is washed twice with 10 ml. of

*5 The acidity of the solution is not more than 0.5N in sulphuric acid.

benzene and is also evaporated to almost dryness,— Niobium-95 fraction. After adding appropriate amount of water, a portion of each of fractions is dried on Mylar films to make point sources for the countings.

Using benzoyltrifluoroacetone : To 2~3 ml. of zirconium- niobium-95 mixture solution[*5] 3 ml. of 1*N* sulphuric acid, 1 ml. of 1 % hydrogen peroxide and 3~4 ml. of water are added, and the solution is shaken with 10 ml. of 1*M* benzoyltrifluoroacetone-benzene solution for 1 hour. The aqueous layer is washed with benzene,

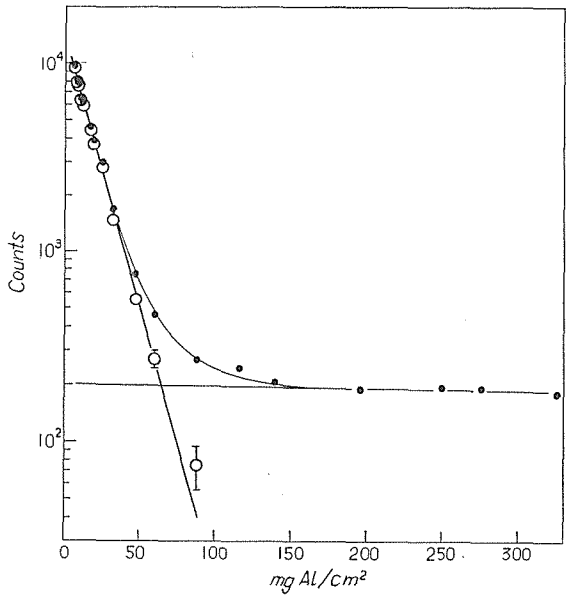

Fig. 6. Absorption curve of ^{95}Zr fraction [Trifluoroacetylacetone-benzene extration].

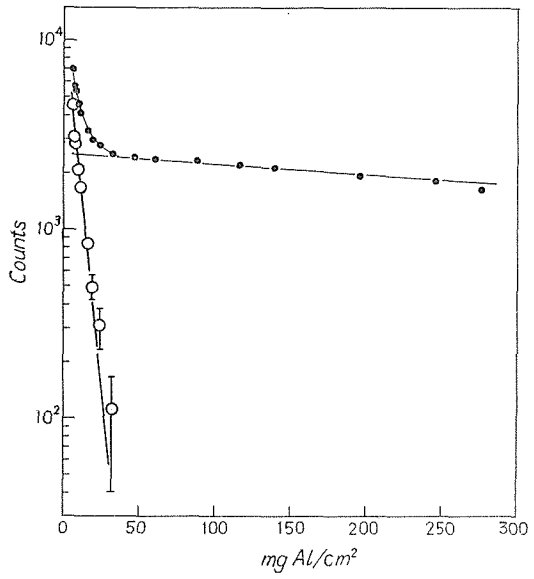

Fig. 7. Absorption curve of ^{95}Nb fraction [Trifluoroacetylacetone-benzene extraction].

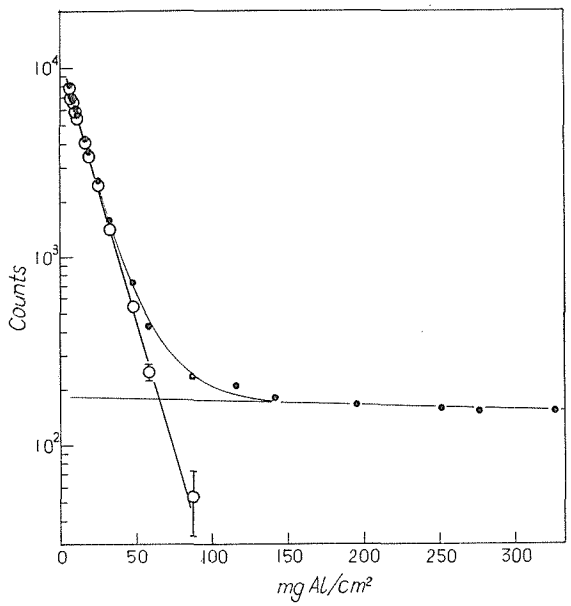

Fig. 8. Absoption curve of ^{95}Zr fraction [Benzoyltrifluoroacetone-benzene extraction].

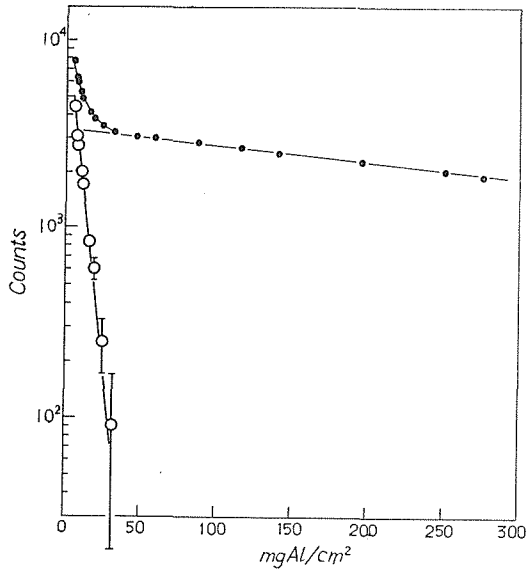

Fig. 9. Absorption curve of ^{95}Nb fraction [Benzoyltrifluoroacetone-benzene extraction].

while the organic layer is washed with 0.3 N sulphuric acid containing hydrogen peroxide, and zirconium-95 is then stripped with 5 ml. of 6 N sulphuric acid. The counting sources of zirconium-95 and of niobium-95 are prepared by the above described manner.

The absorption curves of beta-rays obtained with those sources were shown in Fig. 6~Fig. 9. The curves indicate that the extraction using trifluoroacetylacetone or benzoyltrifluoroacetone can be applied to the separation of zirconium-

95 as well as the acetylacetone extraction.

Because the extraction separation of zirconium and niobium is carried out in mineral acid medium by using trifluoroacetylacetone or benzoyltrifluoroacetone, not only the pH adjustment is not necessary, but also niobium-95 can be separated as a salt-free state, as mentioned above. However the extraction using benzoyltrifluoacetone shows such inconveniences that relatively long shaking is needed to the complete separation, and the extractability of zirconium and the decontamination factor of niobium are somewhat lower than in the case of trifluoroacetylacetone, although the former reagent is more stable than the latter one. Besides the above described expedience the trifluoroacetylacetone procedure has some advantages like acetylacetone one : the distribution rapidly reaches the equilibrium ; zirconium is readily back extracted into dilute sulphuric acid ; and the reagent is easily decomposed by fuming with sulphuric acid or with perchloric acid.

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